



REVIEW ARTICLE

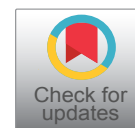
A Review of Environmental Contamination by Organochlorine and Organophosphorus Pesticides in Egypt

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Introduction

All pesticides are potentially toxic to all sorts of life and some are even classified as probable human carcinogens, neurotoxics and endocrine system disruptors. The toxicity level of a pesticide depends on the lethal dose (LD) of the chemical, the length of exposure, and the route of entry or absorption by the body. There are many different pesticides in use today with very different modes of action and levels of toxicity. To protect the public, WHO has developed a hazard classification system which is used to label all pesticide containers to warn users of the acute hazards associated with each product. This hazard system is based on the LD50 for the pesticide in rats under either oral or dermal exposure conditions [1].

Chlorinated pesticides tend to be chemically stable under aerobic surface conditions. Due to their relative insolubility, most OCPs are strongly adsorbed onto suspended particles in water. Their immobility and persistence can lead their accumulation in soils where seemingly moderate applications of pesticides have been applied. Aldrin has been recovered after six years, both as traces and more abundantly as the metabolite, dieldrin. DDT has been recovered up to 30 years after deposition [2]. The chemical stability of many members of the group (or of their immediate and often toxic metabolites) is high because their molecules are constructed, entirely or largely, from C-C, C-H and C-Cl bonds which tend to be chemically

inactive under normal environmental conditions. In consequence, traces of organochlorine compounds can be found in air and water throughout the world. OCPs are a major group of pesticides, used in agriculture, public health, industry and the household. OCPs are widespread environmental contaminants in various environmental matrices because of their persistence and stability. The Cl atoms on the organic moieties in the OCPs make these compounds very stable in the environment. This persistence can be advantageous for the control of pests such as termites around buildings. The lack of biodegradation and the high lipid solubility of these OCPs, however, have led to problems with the accumulation of these compounds in animal tissues. For example, the concentration of chlordane, are much higher in fish tissues than they are in the water in which the fish are living via the "bioconcentration" process [1]. Exposure to OCPs may cause some acute and chronic illnesses. Symptoms of acute poisoning can include tremors, headache, dermal irritation, respiratory problem, dizziness, nausea, and seizure. OCPs are also associated with many chronic diseases. Studies have found a correlation between OCP exposure and various types of cancer, neurological damage (several organochlorines are known neurotoxins), Parkinson's disease, birth defects, respiratory illness, and abnormal immune system function [3]. Many OCPs are known or suspected hormone disruptors, and recent studies show that extremely low levels of exposure in the womb can cause irreversible damage to the reproductive and



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immune system of the developing fetus [3]. OCPs tend to accumulate and biomagnify in food chain, reaching higher concentrations in top carnivores. Thus, these persistent chlorinated compounds can cause adverse health effects in organisms that are higher up in the food chain, such as birds. Once the ecological impact of these pesticides was recognized, they were banned from use in many countries, including Egypt. They are still used in some developing countries, though, because of their effectiveness in controlling diseases and for increasing food production. They also are safer for humans to handle than the newer insecticides that were developed to take their place, the organophosphate and carbamate insecticides.

Organophosphorus (OP) compound consist of a group of roughly 250 chemicals manufactured all over the world. Approximately 140 of these compounds are pesticide, and the remaining are mainly industrial chemicals used as flame retardants, plasticizers and industrial hydraulic fluids and solvents [4]. OPs pesticides are much less persistent in the environment, but are toxic to non-target creatures such as aquatic organisms, birds and some beneficial insects. OP compounds can be considered as derivatives of inorganic phosphorus compounds in which one or more hydrogen atoms have been replaced by organic groups. OP insecticides are normally esters, amides, or thiol derivatives of phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids. Most are only slightly soluble in water and have a high octanol/water partition coefficient and low vapour pressure. They are generally among the most acutely toxic of all pesticides to vertebrate animals. They are also unstable and therefore break down relatively quickly in the environment [5]. By the late 1970s, the use of OPs began to overtake the OCPs which included DDT. While OCPs were relatively safe to use, their problem was its persistence in the environment and detection in the human food chain. OPs on the other hand are more acutely toxic, but, do not persist in the environment beyond a few months. So with the replacement of OCPs by OPs, it could lead to safer food for the consumer but at the expense of the pesticide operator. The persistence of these compounds in the marine environment depends on the different degradation pathways including chemical, photochemical and biological processes. Hydrogen ion concentration, temperature, salinity, and microorganisms affect their persistence in the marine environment [4]. In general the half-life of these compounds in seawater range from few hours to few weeks (12 hours to 30 days) [6-10], faster degradation of these compounds was observed in seawater compared to fresh water which might result from the hydroxide-catalyzed hydrolysis which predominates in the marine environment. Photodegradation studies in water using either sunlight or UV irradiation have shown a variety of photo alteration products, e.g. oxo derivatives and

different phenols which may be even more toxic than the parent compounds. OP compounds are toxic because of their action on the nervous system. OP pesticides inhibit the enzyme acetylcholinesterase (AChE), leading to accumulation of toxic levels of endogenous acetylcholine in nervous tissue which disturbs the correct functioning of the nervous system [11].

Nevertheless pesticides will continue to play a major role in the production of food and fiber especially in the developing countries. Reduction of pesticide usage would increase production costs and would also influence the quality of agriculture products. Some of the pesticides are also essential for protecting human and animal health. In Egypt, as in many other agricultural countries, pesticides are widely used to control pests of field crops. Nearly all pesticides are readily soluble in plant oils and waxes; this common property places them all under suspicion as food contaminants. Determination of pesticide residue is considered a national goal to protect health and limit environmental pollution. Environmental pollution by pesticides residues is a major environmental concern. Pesticides are usually applied by hand, and/or large mechanical sprayers, hence, it is inevitable that during pesticide application, various amounts of these toxic substances reach adjacent vegetation, wildlife, soil and water. In this way the impact of pesticides is felt far beyond the designated target area. It has been estimated by Pimental and Goodman [12] that only 5% of the pesticides reach the target pests. Hence, about 95% of the used pesticides end up in other parts of the environment. Most of pesticides ultimately find their way into rivers, lakes, ponds, and other water bodies [13] but also to the organisms which contribute to the food of fish [14].

Egypt is the most populous country in the Arab world. The majority of the 100 million inhabitants of Egypt live in crowded cities and villages along the narrow green strip of land beside the River Nile and north delta around the capital, Cairo. In this densely populated and limited area, about one million metric tons of commercial pesticides were used [15].

Aims of the Study

The present study was conducted to portray some of the side effects of using chlorinated hydrocarbons and organophosphorus insecticides on man and his environment in Egypt. Both groups of insecticides have been extensively used for decades to control crop pests and also to control disease transmitting insects. The contribution of using both insecticides groups in food security and minimizing the spread of some particular diseases is well documented. One major aim of the current study is to portray some of the negative impacts encountered through the long history of using insecticides to help adopting a sustainable pesticides use program, avoiding the pitfalls of the past pest

control history.

Materials & Methods

The present study is based on screening a vast number of literature that documented some of the impact of the use of organochlorine and organophosphorus insecticides in Egypt. Particular emphases were made on the collection of information of contaminated water bodies because of the special vulnerability of these ecosystem to contamination. Collected information were scrutinized to ensure the validity of the results and conclusions reached. The literature body was selected to reflect contamination level at various time stages, where thorough comparison and recommendations can be concluded. In some particular cases contact was made with authors to clear up, and/or understand particular points. Results obtained from local Egyptian environment were compared with similar work conducted in some developed and developing countries to ascertain how to compare Egypt's pesticides contamination level with other countries.

Results

Use of OCPs in Egypt

Concern over the environmental and health effects related to pesticides use began in the 1950s with the OCPs including DDTs, lindane, endrin and other organochlorine insecticides, which were used extensively for agricultural control of insects, mainly the cotton leaf worm and bollworms. More than 13000 tons of DDT, 45000 tons of toxaphene, 10500 tons of endrin and 11300 tons of lindane were used in Egypt in the period between 1952 and 1981 [16]. The reported major OCPs used in Egypt during a 30-year period were toxaphene (1955-1961), endrin (1961-1981), DDT (1952-1971) and lindane (1952-1978). The continuous shifting from one compound to another was mainly attributed to the development of resistance of cotton leaf worm [17]. OCPs have serious environmental and health hazards. Based on the reports of their toxicity and adverse harmful effects to wildlife and humans, many OCPs were banned or restricted from use or trade by the ministry of agriculture. Since 1980 DDT and lindane have been officially prohibited from agricultural use in Egypt, and in 1996 a ministerial decree prohibited the import and use of 80 pesticides including aldrin, dieldrin, endrin, chlordane, heptachlor, DDT, toxaphene, mirex, lindane, endosulfan, pentachlorophenol, heptachlor epoxide, as well as 20 other chlorine containing pesticides and organometallics. However, organochlorine pesticides are still widely used in Egypt [18-21]. Industrialization and urbanization, unaccompanied by productive legislation, are occurring rapidly, leading to dangerous increases in environmental pollution [22] and ongoing detection of organochlorine in human population, in fish water, and soil samples [19-21,23-27]. Generally, surface water may be contaminated by pesticides, either

Table 1: Residues of organochlorine hydrocarbon insecticides in freshwater from Alexandria City^a.

Pesticide	Concentration (ppb)			
	Canals raw water	Plants treated water	Tap water	waste water
HCB	0.39	ND	0.1	0.19
Lindane	0.34	0.19	0.29	0.63
Heptachlor	0.7	0.1	0.12	0.19
p,p`-DDT	0.65	0.47	0.47	0.95
o,p`-DDT	0.95	ND	0.95	0.25

ND = Not detected; ^aAdapted from El-Sebae and Abu El-Amayem [29].

Table 2: Residues of organochlorine insecticides in water and sediment of LakeMaruit (North Alexandria)^a.

Sample	Concentration (ppb)	
	Lindane	p,p`-DDT
Water	1.65-2.76	2.54-6.39
Sediment	52.8-142.8	318-982

^aAdapted from Abu El-Amayem, et al. [30].

directly by application into the water or indirectly from the discharge of waste water and/or agricultural runoff. Further contamination may arise from drift or washing of spraying equipment [28]. Drainage water from the pesticides treated land is pumped into several major drains that finally discharge their waters into the river Nile or lakes where they cause substantial fishery losses. A brief account about OCPs residues in Egyptian aquatic environment have been reported by several studies for instance; El-Sebae and Abu El-Amayem [29] recorded detectable concentrations of some OCPs in freshwater samples (raw water, treated water, tap water and wastewater) from Alexandria City, Egypt. Generally, tap water contained pesticide residues higher than those found in the water taken from the plant after treatment (Table 1).

Abu El-Amayem, et al. [30] determined the level of lindane and p,p`-DDT in water and sediment sample collected from Lake Maruit, north Alexandria. Sediment samples contain 52.8-142.8 ppb lindane and 318.0-982.0 of p,p`-DDT (Table 2). Aly and Badawy [31] determined the organochlorine residues in fish samples from the River Nile. All samples were collected during August 1981 to July 1982 from six stations selected in river Nile and two canals located from Aswan to Cairo. The results of this study demonstrated that levels of DDT and its metabolites p,p`-DDD and p,p`-DDE were much higher than the OCPs especially in agricultural area. The total DDT and its metabolites reached highest value in case of one sample obtained from Abou-El-Ghiet canal (223.8 $\mu\text{g kg}^{-1}$). El-Mahmodia canal showed highest concentration mean of o,p`-DDT (141.42 $\mu\text{g kg}^{-1}$). Endrin was the second most common residue begin detected with the exception of one sample from El-Mahmodia canal, its residues ranged between not detected to 86 $\mu\text{g kg}^{-1}$. Residues of BHC were found in all samples at low concentrations, its residues ranged between 0.5 $\mu\text{g kg}^{-1}$ to 30 $\mu\text{g kg}^{-1}$. Lindane was found in all samples at low

concentration but higher than BHC. The lowest residue was reported at El-Mahmodia canal ($0.6 \mu\text{g kg}^{-1}$), while the highest concentration was found in the Abou-El-Ghiet canal ($18.6 \mu\text{g kg}^{-1}$).

Macklad, et al. [32] determined OCPs residues in some fish samples from lake Mariut and Alexandria Hydrodrome. The result showed that DDT and its metabolites (DDE and DDD), HCH and endrin were the major compounds found in *Mugil* and *Tilapia* fish species.

Saad, et al. [33] determined the DDT group in surficial sediment samples from three shallow Nile delta lakes (Lake Mariut, Nozha hydrodrome and Lake Manzala). The date of sample collection was 1968 for Lake Maruit and 1970 for the other two lakes. Total DDT concentrations in composite sediment samples were higher in Lake Manzala (877 ng g^{-1}) than the other two Nile Delta lakes (30 and 54 ng g^{-1} for Lake Maruit and Nozha hydrodrome, respectively).

El-Dib and Badawy, [23] studied the levels of some OCPs in the river Nile at five sites, namely Cairo, Al-Mansora, Demitta, Kafr El-Ziate and Rosetta. Residues of BHC, lindane, endrin, DDT and its analogues were detected in all water samples. Chlordane, *o,p*-DDT and aldrin were not detected. In general, residue levels of the studied compounds followed the order DDT > endrin > lindane > BHC. Highest concentrations of BHC, lindane, endrin, *p,p*-DDT and its metabolites were found in samples collected from Kafr El-Ziate. At that location a refinery and pesticide packing firms discharge their wastes into the river.

Abdel-Razik, et al. [34] determined OCPs residues in water samples collect from El-Abbasa drinking water station before and after purification treatment during the period February through June, 1986. Residue analysis revealed that the pesticides detected in purified and nonpurified water were α -BHC, lindane, aldrin, dieldrin, endrin and *p,p*-DDT. It was noticed that the mean value of α -BHC, lindane and aldrin were comparatively higher in purified water than in nonpurified water. Moreover, the average level of dieldrin, endrin and *p,p*-DDT in drinking water were less than in surface water. No residues of chlordane were detected in water samples before and after purification treatment.

Abdallah [35] determined the residue levels of OCPs and PCBs residues in water and sediment samples collected from the river Nile. Seven sites were selected to represent different regions in delta Nile and El-Rayah El-Beheiri. These sites are delta barrage at Cairo, Kafr El-Ziate, Desouk, Edfina, Rosetta, El-Mansora and Demitta. Kafr El-Ziate was the most polluted location showing 1495 ng l^{-1} for water and 7.4 mg kg^{-1} for sediment. However at Rosetta, which is downstream with respect to Kafr El-Ziate, the total concentration of OCPs and PCBs was decreased to reach 473.98 ng l^{-1} for water and 3.8

mg kg^{-1} for sediment. As a general trend residue levels of OCPs in water samples increased in the following order: Kafr El-Ziate (842.47 ng l^{-1}) > Desouk (443.86 ng l^{-1}) > Edfina (424.45 ng l^{-1}) > El-Mansora (394.72 ng l^{-1}) > Rosetta (333.46 ng l^{-1}) > Demitta (181.0 ng l^{-1}) > delta barrage (53.02 ng l^{-1}).

Reports issued by the central Agriculture pesticides laboratory (CAPL) indicate that there were high concentrations of persistent OCPs in samples collected from several drains and irrigation canals [36]. The distribution and residue levels of HCB, lindane, PCBs, *p,p*-DDT and its metabolites in different fish species collected from Egyptian Delta lakes were evaluated in Table 3. Dogheim, et al. [18] recorded the levels of OCPs in fish samples collected from Beni-Suef and Fayom governorate. DDT was the predominant pesticide detected in fish samples. The concentration of lindane, β -HCH and chlordane were 0.59 , 0.435 and $0.059 \mu\text{g kg}^{-1}$. The levels of other OCPs (as average) were heptachlor ($0.56 \mu\text{g kg}^{-1}$), heptachlor epoxide ($0.14 \mu\text{g kg}^{-1}$), aldrin ($0.59 \mu\text{g kg}^{-1}$), dieldrin ($0.61 \mu\text{g kg}^{-1}$) and endrin ($3.34 \mu\text{g kg}^{-1}$). Abdel-Razik, et al. [37] determined OCPs residues in 18 sediment samples collected from the river Nile distributaries and drains at agricultural areas of Sharkia Governorate from February through April, 1986. The analytical data revealed that El-Ghar canal sediments contained the highest level of endrin, chlordane, dieldrin and aldrin pesticides. However, high quantities of *p,p*-DDT, lindane and α -BHC were detected in sediments of El-Aslogy and El-Ebrahimia drains. Bahr El-Dakar and Ekwa drain sediments contained the lowest amounts of all the tested OCPs residues. El-Gendy, et al. [26] reported cyclodiene pesticides (aldrin, endrin and heptachlor) in water samples collected during 1988 from the river Nile in a wide range of values. Higher concentrations were reported at Kafr El-Ziate city and at sites on the Rosetta than on Damietta branch. *p,p*-DDE and γ -HCH isomers dominated the DDTs and HCHs distributions at all locations. Total concentration of cyclodiene pesticide in sediment ranged from below detection limit to 2917 ng g^{-1} dry weight, with decreasing abundance in the order aldrin > heptachlor > endrin. Abou-Arab, et al. [19] studied the distribution of OCPs in the Egyptian aquatic ecosystem (fish, sediment and water). The samples were collected from two catching areas that represent two different models of the aquatic ecosystem (El-Malek-El-Saleh and Manzala Lake). Data showed that DDT and its analogues were predominant in fish samples collected from Manzala Lake. On the other hand, total DDT followed by heptachlor were predominant in fish samples collected from the River Nile. The same OCPs were found in water samples collected from Manzala Lake and the river Nile during the two seasons, winter and summer. The concentrations of pesticides in samples from river Nile were lower than those from Manzala Lake. Pesticide residues detected in sediment samples from Manzala during winter and

Table 3: Levels of some chlorinated insecticides in delta lakes (ng g⁻¹ wet weight)^a.

Location/year	Fish species	∑DDTs	% p,p'-DDT	Lindane	HCB	PCBs	Reference
Manzala							
1982	<i>Mugil cephalicus</i>	21.1	16.3	0.1	0.19	-	Badawy and El-Dib [129]
	<i>Mugil cephalicus</i>	16	55.4	1.07	6.94	-	
	<i>Tilapia sp.</i>	18.5	55.85	0.59	3.59	-	
	Mean	18.5	42.52	0.58	3.57	-	
1990	<i>Mugil cephalicus</i>	15.7	69	2.81	3.28	-	Abou-Donia [130]
	<i>Tilapia sp.</i>	23.2	53	1.93	3.06	-	
	<i>Moran labrex (karous)</i>	21.4	33	2.13	3.04	-	
	<i>Moran labrex</i>	16.8	51.7	0.37	3.12	-	
	Mean	28.7	51.7	1.81	3.13	-	
1992	<i>Clarias anguillaris (catfish)</i>	23.3	0.3	0.19	0.17	3.4	UNEP [123]
	<i>Clarias anguillaris</i>	19.1	ND	0.26	0.19	6.4	
	<i>Tilapia sp.</i>	62.1	0.7	2.3	0.71	13.2	
	<i>Anguilla anguilla (eel)</i>	34.8	0.3	0.92	0.36	7.6	
	Mean	34.8	0.4	0.87	0.36	7.7	
1995	<i>Clarias anguillaris</i>	47.1	3.2	1.57	0.73	7.4	Badawy and Wahaab [131]
	<i>Tilapia sp.</i>	18.4	1.9	1.26	0.45	6.5	
	<i>Mugil cephalicus</i>	25.4	3.7	0.76	ND	10.1	
	<i>Anguilla anguilla</i>	56.4	2.6	2.3	1.2	11.2	
	Mean	36.8	2.8	1.47	0.6	8.8	
IDKU							
1982	<i>Mugil cephalicus</i>	24.8	38.6	2.6	8.23	-	Badawy and El-Dib [129]
	<i>Tilapia sp.</i>	40.2	35.1	4.8	12.72	-	
	Mean	32.5	36.9	3.7	10.48	-	
1990	<i>Mugil cephalicus</i>	18.67	58	2.8	3.28	-	Abou-Donia [130]
	<i>Tilapia sp.</i>	13.19	53	1.93	3.06	-	
	<i>Moran laberx (karous)</i>	26.2	27.1	2.13	3.04	-	
	Mean	19.35	46.2	2.47	3.15	-	
1991	<i>Tilapia sp.</i>	9.03	0.7	0.91	0.16	-	UNEP [123]
Maruit							
1982	<i>Clarias anguillaris (catfish)</i>	17.6	40.3	ND	3.9	-	Badawy and El-Dib [129]
	<i>Tilapia sp.</i>	25.4	14	4.5	8.5	-	
	Mean	21.5	27.2	2.25	6.2	-	
1990	<i>Tilapia sp.</i>	8.4	0	0.44	4.9	-	
	<i>Moran laberx (karous)</i>	11.08	5.4	0.36	2.35	-	
	Mean	9.74	2.7	0.4	3.63	-	
1991	<i>Tilapia sp.</i>	2.97	ND	0.7	0.29	-	UNEP [123]
Permissible limit (mg kg ⁻¹)		2		0.65	0.28	1.3	

ND = Not detectable; ^aAdapted from Badawy [132].

summer followed the same descending order: total DDT > heptachlor > aldrin > lindane > γ -chlordane > β -BHC during the two seasons. During winter, total DDT predominated in all samples, analyzed from the river Nile, followed by heptachlor, aldrin, γ -chlordane, β -BHC and lindane. Meanwhile, during summer, residues were found in the following descending order: Total DDT > heptachlor > β -BHC > γ -chlordane > aldrin > lindane.

Badawy, et al. [27] determined chlorinated hydrocarbons in water from Lake Manzala and associated canals. The results confirm low level of background organochlorine compounds in this area, p,p'-DDT was not detected in samples from Hadous and Bahr El-Baqar canals. However p,p'-DDT was detected in all samples collected from the lake and its concentration ranged from 0.5 to 1.6 ng l⁻¹, with an average value of 1.2 ng l⁻¹. In 1995, a condensed monitoring program was carried out by the Ministry of

Public Work and Water Recourses (MPWWR) to analyze water samples along the River Nile. β -HCH, lindane, aldrin, dieldrin, heptachlor, endrin, p,p'-DDT and its analogous were detected. The highest detected level of DDTs was at Aswan Dam, reaching 1.048 μ g l⁻¹, which is considered slightly above World Health Organization [38] and Egyptian Guidelines of 1 μ g l⁻¹ in the drinking water (Table 4). Dogheim, et al. [39] recorded OCPs in water and fish samples collected from Kafr EL-Ziate governorate. The major pesticides detected were HCHs isomers and p,p'-DDT and its metabolites p,p'-DDE and p,p'-DDD. Osfor, et al. [40] studied the occurrence of OCPs in the Egyptian aquatic ecosystem (fish, sediment and water). The samples were collected from different localities in Manzala Lake and from an area along 10 km of the river Nile. Levels of lindane (13.8 mg kg⁻¹) and endrin (26.5 mg kg⁻¹) were significantly higher in sediment of Manzala lake, while the level of heptachlor

Table 4: Organochlorine insecticides and PCBs in water samples collected from river Nile^a.

Sampling site	Concentration (ng l ⁻¹)					
	∑HCH	∑HCBs	∑DDTs	Cyclodiene	∑OCPs	PCBs
Lake Nasser	650.46	81.3	841.47	20.86	1594.1	59.86
Aswan	220.36	36.66	1048.24	28.5	1333.8	56.38
Kom Ombo	187.71	31.16	1035.25	41.27	1295.4	85.65
Esna	177.62	32.2	586.3	75.37	871.49	15.65
Naga Hamady	123.16	24.56	297.72	40.65	486.09	32.84
Assiut	143.65	28.37	100.56	75.28	247.86	58.46
El-Minia	163.76	30.35	82.42	16.77	293.3	28.58
BeniSuef	285.4	42.85	56.83	26.5	411.58	25.3
Delta Barrage	22	10	2.65	29.75	64.4	8.28
Kafr El-Ziate	249.34	49.65	29.75	415.37	744.16	652.84
Dessouk	166.27	53.56	37.21	186.82	443.86	295.46
Edfina	107.26	77.8	10.133	228.11	423.3	71.76
Rosetta	185.87	16.7	98.51	32.39	333.42	140.52
El-Mansoura	151.01	92.61	102.67	48.43	394.72	32.43
Demietta	26.12	3.9	90.87	65.57	186.46	73.66

∑HCH = α , β and γ -HCH, ∑HCBs = α , β and γ -HCB; ∑OCPs = Total organochlorine pesticides; ∑DDTs = p, p'-DDD, p, p'-DDE and p, p'-DDT; Cyclodiene = heptachlor + aldrin + endrin + heptachlorepoide; ^aAdopted from Abdel Wahaab and Badawy (2004) [133].

(43.2 mg kg⁻¹), aldrin (37.5 mg kg⁻¹), p,p'-DDE (113.5 mg kg⁻¹) and DDT(118.7 mg kg⁻¹) were significantly higher in sediment of River Nile. Boury fish of Manzala lake contained higher levels of heptachlor (1.17 mg kg⁻¹), aldrin (0.21 mg kg⁻¹) and p,p'-DDE (0.030 mg kg⁻¹). The result indicated that lake Manzala and even the River Nile which was used as control are heavily contaminated with chlorinated hydrocarbon (lindane, heptachlor, aldrin, endrin, dieldrin, p,p'-DDE and DDT). Ahmed, et al. [41] monitored residues of lindane, heptachlor, heptachlor epoxide, aldrin, endrin, dieldrin and DDT in rain water, the soil profile and ground water. Heptachlor and heptachlor epoxide were detected in rain water in 1995 and 1996. The total concentration of OCPs detected were 4.7 and 10.6 $\mu\text{g l}^{-1}$ for 1995 and 1996, respectively. Residues detected in ground water were higher than residues reported in many European countries. Moursy and Ibrahim [42] studied the contamination of Manzala Lake by OCPs. The total concentrations of cyclodienes were found in the range 8-21 ng l⁻¹ in water samples. Abbassy [43] studied pesticides drained into north coast of the Mediterranean Sea, Egypt. The water samples collected from the mouths of Edku Lake at El-Madia, north coast of El-Behera governorate, El-Amia drain at El-Tabia, North East coast of Alexandria governorate, and El-Umum drain and Maruit Lake at El-Mex pump station, North West coast of Alexandria governorate. The result indicated that chlorinated pesticide especially DDT and its degradates, DDD and DDE were still detected in surface water in Egypt in spite of its banning since many years ago because of their persistence against degradation and the result is an accumulation in the environment. El-Kabbany, et al. [44] determined OCPs in some water supplies in El-Haram, Giza, Egypt. The water samples were collected from El-Haram region, Giza, canal water supplies (El-Zomor, Abd-el-all land and

Seaside and El-Mansorya), in addition to El-Moheet drainage water. Sixteen OCPs were detected in most of the water samples and the percent of positive samples followed the order drins > total BHC > total DDT > endosulfan > heptachlor epoxide > heptachlor. Yamashita, et al. [45] found low concentration of 8-11 and 11-16 $\mu\text{g l}^{-1}$ of chlordane components in filtered water and suspended solids of the Nile water, respectively, and up to 68 and 39 $\mu\text{g l}^{-1}$ in Manzala costal lagoon. Lower levels of heptachlor were found in the Nile river water, at concentrations of 1.9-4.5 and 1.6-3.6 $\mu\text{g l}^{-1}$ in filtered water and suspended solids, respectively, and up to 7.8 and 3.0 $\mu\text{g l}^{-1}$ in Manzala coastal lagoon. Chlordane has only rarely been reported in Egypt. Low levels of heptachlor have been found in sediments from the Nile River close to Cairo (0.52-0.93 ng g⁻¹ dry weight) and the Manzala Lake (0.01-0.60 ng g⁻¹ dry weight). Mansour and Messeha [46] determined OCPs residues in water and fish samples collected from Qarun Lake, a private fish farm for comparison with the lake and from major canal located in the area of study. OCPs were detected in most samples. The fish from the lake were found to contain lower levels of contaminants as compared with the same species from the fish farm. Zidan, et al. [47] determined OCPs contaminating Nile water and agriculture eco-system at Qalubia governorate. Drainage water samples from El Kanater showed the highest occurrence frequencies with α -HCH, heptachlor, heptachlor epoxide and p,p'-DDE. Abbassy, et al. [48] studied the levels of OCPs in water, sediment and biota samples collected from El Manzala Lake. DDE was detected in higher levels while lindane detected in lower levels in most samples. Abdallah and Gaber [49] studied the contamination by OCPs of water samples collected from different sources in El-Behera governorate, Egypt. All the water samples investigated were found to have detectable amount of OCPs.

Mansour and Sidky [50] studied the contamination of water, sediment and fish samples collected from Lake Qarun and Wadi Ei-Rayan lakes (Egypt). Lindane and aldrin were found in Lake Qarun water at a very low concentration, 0.003 and 0.008 ppm, respectively. Sediment and fish samples from Lake Qarun appeared to be more contaminated with OCPs than the samples from the lakes of Wadi El-Rayan. Marzouk, et al. [51] studied the existence of OCPs residues in different irrigation water sources in Egypt. The water collected from different irrigation water sources, Nile water, ground water, agricultural drainage water, sewage water and treated sewage water, from Taha-nub and El-Gabal El-Asfar, Qalubia Governorate. The mean of all detected OCPs in most irrigation water sources during summer and winter seasons were below WHO, 1992 or EPA, 2002 drinking water guideline. In exception, endrin was high in all irrigation water sources during summer season and in Nile water and agricultural drainage water during winter season. Also, *o,p'*-DDT was higher than permissible limits in all irrigation water sources during summer season. As well as, *trans*-chlordane that was high in sewage water and treated sewage water in summer season in ground water during winter season. Salah El-Dien and Nasr [52] recorded OCPs residues in crayfish samples collected from three villages near Zagazig city, Sharkia Governorate, during summer and autumn, 2003. The obtained results revealed that the mean values of OCPs residues were 0.522, 1.116, 4.5, 1.117, 0.5, 5.541, 2.5, 0.288, 0.066, 27.5 and 1.805 ng g⁻¹ of α -HCH, β -HCH, γ -HCH, aldrin, endrin, heptachlor, heptachlor epoxide, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT and γ -chlordane, respectively. δ -HCH, dieldrin and *p,p'*-DDD were not detected in all the examined samples. El Nemr and Abdallah [53] analyzed ten OCPs residues in four species of fish (Bouri, Denis, Moza and Mousa), collected from four Egyptian governorates (South Sinai, Port-Said, Suez and Damietta). The highest concentration of pesticides was recorded in Damietta governorate fish (20-211 ng g⁻¹ of wet weight) and the *p,p'*-DDE dominated over the other *p,p'*-isomers in all studied fish, while dieldrin was the dominated in the studied cyclodiene compounds. Chlordane was not detected in any studied fish. The level of OCPs contamination in fish from the studied governorates is relatively low and should not pose a health risk to consumers. Said and Hamed [54] investigated the pollution by OCPs in water and fish samples collected from El-Temsah and Bitter lakes of the Suez Canal. The results indicate the presences of total DDTs, total cyclodiene and total HCHs in surface water with ranges; 2.76-13.88, 3.99-16.39 and 0.39-1.25 ng l⁻¹, respectively. Total DDTs concentrations were ranged from 161-3100 ng g⁻¹ (wet weight) with an average of 1087 ng g⁻¹ (wet weight), while total HCHs concentrations ranged from 30-1145 ng g⁻¹ (wet weight) with an average of 316 ng g⁻¹ (wet weight) recorded in the fish samples. Concentrations of OCPs recorded in both of water and fish samples of the investigated area

can be ranked in the order; total cyclodienes > total DDTs > total HCHs. Abdel-Halim, et al. [55] studied the residue level of OCPs in the aquatic environment (water, sediment and fish) of the drainage canal surrounding a pesticide factory at Damietta governorate. HCH isomers, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, aldrin, dieldrin, endrin and heptachlor epoxide were detected in most samples. Sallam, et al. [56] determined OCPs residues in sediment samples collected from different location of river Nile from Aswan to Damietta governorate during December 2004 to January 2005. Upper Egypt governorate recorded higher concentration of OCPs pesticide residues in sediment samples than the north Egypt governorate. Rashed, et al. [57] estimated OCPs in water and fish samples collected from ten locations at Giza governorate. OCPs were the major pollutants in fish samples and detected in 30% of the samples. Nasr, et al. [58] assessed the concentration of organochlorine pesticides (OCPs) in aquatic environment at El Menofiya Governorate to explore the effect of sampling area and different matrix. The concentration of pesticides residue in the analysed water samples followed the following descending order *p,p'*-DDE > *p,p'*-DDD > endosulfan > endrin > heptachlor epoxide > aldrin > α -HCH > β -HCH > γ -chlordane > heptachlor > *p,p'*-DDT. DDT and its metabolites *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT were detect at high levels in sediment sample. The *p,p'*-DDE residue were the most abundant in fish sample.

Discussion

In spite of toxicity and adverse human effects of OCPs, many developing countries continue to use these compounds for crop protection and vector control because of their effectiveness and low cost [59]. Aryamanya-Mugisha [60] reported that eighty tones of DDT per year is used against cotton pests and for controlling mosquitoes in Uganda, and approximately three hundred ninety two tons of dieldrin per year is used for controlling banana weevils. Other OCPs used in Uganda include lindane, aldrin, chlordane and heptachlor. Mohapatra, et al. [61] reported that OCPs are used in large quantities in India because of their effectiveness and low cost. Some of these compounds (e.g. DDT) have been banned for use in agriculture but are still begin used for vector control in public health programs. Brunetto, et al. [62] reported that DDT is used in Venezuela in farming activities as well as in programs of public health, as it is a powerful low cost insecticide. Minelli and Ribeiro [63] reported that most OCPs have been eliminated in Brazil, but DDT and HCH continue to be permitted in the control of disease carrying vectors. Levels of these pesticides were detected in blood serum of malaria control sprayers. Barlas [64] stated that in spite of use of all OCPs has been prohibited in turkey by a decision made by the Turkish government in 1980s; a lot of OCPs and their degradation products were detected at high levels in water and sediment samples.

The main reason of OCPs contamination can be related to the still widely and illegal use of OCPs in agriculture. In Vietnam, the prohibition of these substances was first issued in 1993, but some studies showed that DDTs were detected in their highest concentration [65]. In Taiwan, a recent study showed that there still exist a variety of OCPs residues in the rivers which DDT and HCHs were the dominant OCPs compounds [66]. In china, OCPs were found in various environmental matrices [67]. Even developed countries including Germany, the prohibition of OCPs was effective 25 years ago, but DDTs were still detected in canal waters [65]. In USA, Europe (Spain, Russia) as well as Asia (China), the presences of OCPs in surface waters, sediments, fish, biota and vegetations have been investigated in detail [67-70]. In Africa, including Nigeria, rapid urbanization as well as severe pest problems, weeds, rodents, locusts, grain eating birds have increased reliance on the use of pesticides. OCPs are cheap form of insecticides and are widely used [71]. Colborn, et al. [72] recorded that OCPs have reproductive and endocrine-disrupting effects. Furthermore, OCPs may act as environmental oestrogens causing disruption in the normal functioning of hormones and may cause breast cancer in humans, posing a significant threat to the ecosystems [73]. The exposure to these compounds in the environment cause abnormal thyroid function in birds and fish, decreased fertility in birds, fish, shellfish and mammals and decreased hatching success in fish, birds, alteration of immune function in birds and mammals. These deleterious health effects have been observed in many areas where the presence of multiple man-made chemical, such as byproducts of industrial chemical synthesis and pesticides. The chemical properties of OCPs, such as lipophilicity and persistency, lead to bioaccumulation of these compounds in the fatty tissues of biological specimens and to biomagnifications throughout the food chain, resulting in a high degree of contamination in top-predators [74,75]. The concentration of OCPs residues in human milk has been the subject of many studies due to its importance as the first food for the newborn child. Although food intake is the main route of exposure, inhalation and dermal routes might have importance for mothers living in countries where sanitary actions are the main source of contamination. With the growing interest in breast feeding, the nature and source of contamination by pesticide still remain questionable, as the transfer of pesticides to breast milk depends on their concentration in the serum of mother and their properties [76]. The concentration of pesticide residues in human milk, vary considerably from one pesticide to another, from country to country and were influenced by factors such as legalization and the culture of society and diet. Dogheim, et al. [39] analyzed OCPs residues in human milk collected from Kafr El-Zayat general Hospital from 31 lactating mothers and 11 samples collected from Cairo Abo El Rish pediatric Hospital. The

mean total HCH isomer in samples from Cairo (193.44 ppb) is higher than samples from Kafr El-Zayat (115.97 ppb). The β -isomers is found in high frequency in both governorates, indicating a continuous degradation of the other 2 isomer (α , γ -isomer) to the more persistent one.

The levels of OCPs in 60 human milk samples, from 20 Egyptian governorates, were determined. The main detected compounds were p,p'-DDE and lindane. The mean values for p,p'-DDE, lindane, endosulfan (I) and p,p'-DDT levels in the milk samples of the 20 governorates studied were 21.37, 8.42, 4.84 and 2.93 $\mu\text{g/L}$, respectively [77].

In a following study, p,p'-DDE (46-156 ng/g whole milk) and p,p'-DDT (3-32 ng/g whole milk) were among the most abundant OCPs residues in 292 mother's milk samples collected from 10 Egyptian governorates representing rural, metropolitan and newly reclaimed desert areas [78]. The percentage of samples exceeding the acceptable daily intake for children (ADIs) set by the FAO/WHO ranged from 7% to 48% in all governorates. Higher percentages of unacceptable samples were recorded in Menofiya and Kaliobia governorates, which may be attributed to the higher agricultural activity in the Delta region. Sharaf, et al. [79] determined the residues levels of OCPs in breast milk, the maternal serum, umbilical serum and abdominal adipose tissue of 38 women giving birth by cesarean section at Kasr El-Eini hospital, Egypt. The distribution of OCPs in the four types tissues revealed that endrin, DDT and its derivatives followed by dieldrin, were the main contaminants. Results indicated positive high correlation between concentrations of DDD and DDE in breast milk and adipose tissue and another positive correlation between concentration of endrin and dieldrin, in breast milk and maternal serum. Many studies have used blood rather than adipose tissue because blood is the most accessible matrix for assessing pesticide residues concentrations in humans. Organochlorine chemicals are among the most persistent environmental contaminants. Some of these chemicals, including DDT, DDE and PCBs, have been suggested to be significantly important in the etiology of breast cancer [80,81]. Various investigations have been performed to evaluate the involvement of these chemicals in initiating breast cancer. Moysich, et al. [81] suggested that an increase in the risk of postmenopausal breast cancer is associated with environmental exposure to PCBs and Mirex, an organochlorine insecticide. Dorgan, et al. [82] found that females with higher levels of hexachlorobenzene, an organochlorine insecticide, in their blood serum were at twice the risk of breast cancer compared with those with low hexachlorobenzene level. However, there was no evidence of a dose-response relationship, and the association was limited to females whose blood was collected close to time of diagnosis. Breast cancer is a major public health concern. According

to Moller, et al. [83], it constitutes about 33% of all tumours affecting females, with an estimated 135,000 new cases and 58,000 recorded deaths per year in The European Union. In Egypt, Abou El Nasr and Botrous [84] mentioned that breast cancer constitutes 27% of all reported malignancy cases. In a study conducted in Alexandria, Egypt, El Sebae and Soliman [85] revealed that breast cancer is the most frequent type of cancer affecting females population.

Surface waters frequently are contaminated by applied pesticides, which wash into streams and lakes where they cause substantial fishery losses. Thus, high pesticide concentration in water directly kills fish; low dosages primarily kill small fish fry. Also, pesticides eliminate aquatic insects and other small invertebrates, which are food for fish. OCPs residues in aquatic environment have been reported by several studies for instance; DouAbul, et al. [86] determined the residues of OCPs in shatt al-Arab River. The average concentration of Σ DDT, endrin and dieldrin in the edible portion of the cyprinid (*Barbus xanthopetrus*) were 21, 4 and 2 $\mu\text{g kg}^{-1}$ wet weight, respectively. Mean values of Σ DDT, endrin and dieldrin in surface sediments were 5, 40 and 20 $\mu\text{g kg}^{-1}$ dry weight, respectively. Shrimps sampled from the shatt al-Arab River were found to contain residues of o, p'-DDD only with an average concentration of 2 $\mu\text{g kg}^{-1}$ wet weight. Cocchieri and Arnese [87] reported that DDT and its derivatives (p, p'-DDD and p, p'-DDE) predominated and recorded in fish from southern Italian rivers. The mean concentrations were 0.18 ppm, 2.6 ppm and 0.085 ppm. The detected range values of lindane were ranged between 0.005 to 0.008 ppm, heptachlor from not detectable to 0.005 ppm, and endosulfan from not detectable to 0.008 ppm. DouAbul, et al. [88] determined the residues of OCPs in Tigris-Euphrates-shatt al-Arab delta. The conclusions of this study were indicated that the Euphrates River is the major source of pesticides in the dissolved form. While the Tigris river contributed pesticides mainly in the particulate form to the shatt al-Arab River. The sediment of the river was the largest reservoir of OCPs, where more than 80% of the studied contaminant residue. Nayak, et al. [89] reported that OCPs residues were found in water samples in almost all the sampling point along both the banks of the river Ganga. The results also revealed that the river water was polluted by pesticides mainly in western bank i.e. ghat region (highest HCH in Rajendra Prasad ghat, DDT and endosulfan in Kedar ghat) than the cultivated eastern banks. Matin, et al. [90] studied the contamination of water samples from the different regions of Bangladesh with OCPs during 1992-1995, both before and after the banning of the use of OCPs. The result indicate slight contamination of some of the water samples of both surface and underground sources with residues of DDT, heptachlor, lindane and dieldrin. Heptachlor was found in surface and ground water at levels well above WHO-recommended limits. Wu, et al.

[91] analyzed the persistent OCPs in surficial sediment samples from seven large Chinese river/estuary systems. Concentrations of HCH were low in most samples except the Zhujiang River where the concentrations were one order of magnitude higher than for other rivers. The level of DDT were relatively low in sediments from north Chinese river/estuary systems while the value of DDT were high in south China. Mortimer [92] quantified OCPs in intertidal burrowing crabs (*Australoplax tridentate*) and a portunid (*Scylla serrata*) sampled from estuaries on the east coast of Australia between Cairns and Brisbane. Residues of dieldrin, heptachlor epoxide and DDT (principally metabolites DDD and DDE) occurred at most locations reflecting the historical use. Chlordane and endosulfan were only detected in crabs in the urban Brisbane area.

Lee, et al. [93] determined the residue of OCPs in 62 sediment samples from Kyeonggi bay and nearby area in the west coast of Korea. The concentration of chlordanes and DDTs showed a distinctive gradient of contamination between inner and outer sites of Incheon North harbor, whereas HCHs were uniformly distributed at most sites studied. The dominant OCPs in sediments were β -HCH among HCH compounds, *trans*-chlordane among chlordane compounds, and p,p'-DDD among DDT compounds. Gilliland, et al. [94] determined concentration of OCPs in water, sediment and green frogs in wetlands of southwestern Michigan. Concentrations of all individual OCPs in tissue were less than 6 ng g^{-1} wet weight. Zhou, et al. [95] analyzed 18 OCPs in samples of sub-surface water, suspended particulate matter and surface sediments collected from Daya Bay, China. The levels of total OCPs were in the range 143.3-5104.8 ng l^{-1} in water and from 2.43-86.25 ng g^{-1} dry weight in sediment. The level of total HCHs in water varied from 35.5 to 1228.6 ng l^{-1} , whilst in sediments they ranged from 0.32 to 4.16 ng g^{-1} dry weight. For the sum of DDTs, their levels were in the range 26.8-975.9 ng l^{-1} in water, and 0.14-20.27 ng g^{-1} dry weight in sediments. Ratios of DDT/(DDE+DDD) in water and sediments indicate recent inputs of such chemicals into the bay.

Barlas [64] studied the contamination by OCPs and their metabolites of water and sediment samples collected from the inner Anatolia lakes to determine the present contamination level and accumulation pattern. OCPs residues in sediment samples were generally higher than residues levels in water samples. α -HCH, β -HCH, heptachlor epoxide, aldrin o,p'-DDT, o,p'-DDD and p, p'-DDT were detected at high levels in sediment samples. Kajiwar, et al. [96] determined OCPs in five species of sturgeons collected from costal water of Caspian Sea in Kazakhstan, Azerbaijan, Turkmenistan and Iran during 2001 and 2002 to understand their status of contamination and accumulation features. Among OCPs examined, concentrations of DDTs were predominant in all the sturgeon samples with

concentration ranging from 73 to 31,000 ng g⁻¹ on lipid weight basis. Sapozhnikova, et al. [68] determined OCPs concentration in sediment and fish collected from Salton Sea, the largest manmade lake in California. Sediment sample were taken during 2000-2001 and fish sample were collected in May 2001. ΣDDT observed in sediments ranged from 10 to 40 ng g⁻¹ dry weight. DDT/DDD ratios in sediment and fish tissue of the northern sea in 2001 indicated recent DDT exposure. Lindane, dieldrin and DDE concentration detected in sediments exceeded probable effect levels established for fresh water ecosystem. ΣDDT concentrations detected in fish tissues were higher than threshold concentration for protection of wildlife consumers of aquatic biota. DDE concentrations in fish muscles tissue were above 50 ng g⁻¹ concentration threshold for the protection of predatory birds. Falandysz, et al. [97] quantified OCPs residues in perch sampled at three sites in the Odra/Oder river estuary in the south-western part of the Baltic Sea, in 1996-1997 to evaluate the status of contamination. All samples of muscle tissue examined contained detectable amounts of OCPs. Kishimba, et al. [98] assess the level of pesticide residues in water, sediment, soil, and some biota collected from different parts of Tanzania. DDT and HCH were dominant in all the studied areas. In the former areas, level of ΣDDT in water, sediments and soil were up to 2 µg l⁻¹, 700 µg kg⁻¹ and 500 µg kg⁻¹, respectively, while those of ΣHCH were up to 0.2 µg l⁻¹, 132 µg kg⁻¹ and 60 µg kg⁻¹, respectively. The levels in aquatic biota were much higher than those in the water most likely due to bioaccumulation. In the former storage area at Vikuge the levels of pesticides in topsoil were alarmingly high. Their concentrations were up to 282,000 mg kg⁻¹ dry weight for ΣDDT and up to 63,000 mg kg⁻¹ dry weight for ΣHCH. Kurt and Ozkoc, (2004) [99] determine levels of OCPs in mussels and seawater from the Mid-Black Sea Coast of Turkey. In mussel samples, the most common pollutants in terms of average concentration per g of wet weight, were DDT (max. 1800 pg g⁻¹, min. 240 pg g⁻¹) and its metabolites DDD (max 5400 pg g⁻¹, min. 240 pg g⁻¹) and DDE (max. 2800 pg g⁻¹, min. 70 pg g⁻¹). Also, dieldrin, heptachlor were notable contaminants in the mussel samples. The data showed that even though the usage of OCPs in turkey was banned, there may still be illegal usage. Naso, et al. [100] analysed edible tissues from 10 marine species, collected from the Gulf of Naples in the southern Tyrrhenian Sea (Italy) between February and July 2003, for the presence of OCPs hexachlorobenzene and DDTs (p,p'-DDT, p,p'-DDE and p,p'-DDD). The level of DDTs ranged from below the detection limit to 2095.5 ng g⁻¹. Pazou, et al. [101] studied the contamination of fish by OCP residues in the Quémé river catchment in the republic of Bénin. DDT, its metabolites and isomers were the most frequently identified pesticides in fish; α-endosulfan, β-endosulfan, dieldrin, telodrin, lindane and octachlorostyrene were also detected. Concentration of pesticide residues in fish ranged from

0 to 1364 ng g⁻¹ lipid. Pazou, et al. [102] studied the contamination of sediment samples collected on nine location along the Quémé river in the republic of Bénin. OCPs identified in sediment samples include p, p'-DDD, p, p'-DDE, p, p'-DDT, o, p'-DDD, α-endosulfan, β-endosulfan, endosulfan sulphate, α-HCH, β-HCH, lindane, aldrin, dieldrin, endrin, telodrin, isodrin, *cis* and *trans*-heptachlor epoxide, hexachlorobenzene and octachlorostyrene. Sankar, et al. [103] determined the level of OCPs residues in fish samples collected from five different locations from the Calicut region, India in order to elucidate the status of these chemical contaminants in fish and shellfish meant for human consumption. The highest concentration of OCPs detected in edible portion of fish were 10.47, 70.57 and 28.35 ng g⁻¹ wet weight, in marine, brackish water and freshwater, respectively. HCH and heptachlor epoxide formed the major share of OCPs in the marine fish while HCHs contributed to the major share in the freshwater and brackish water fish. The DDT (sum of DDT and its metabolites) ranged from 0.05 to 8 ng g⁻¹ in the samples irrespective of habitat. Henry and Kishimba [104] determined the pesticide residues in Nile tilapia (*Oreochromis niloticus*) and Nile perch (*Lates niloticus*) collected from fish landing stations in nine riparian districts on Tanzanian side of Lake Victoria. The residue levels in the fish fillet were up to 0.03 and 0.2 mg kg⁻¹ fresh weight of DDT and endosulfan, respectively. The detection of higher level of p, p'-DDT than the degradation products (p, p'-DDD and p, p'-DDE), and higher level of endosulfan isomers (α and β) than sulphate, in fish samples, implied recent exposure of fish to DDT and endosulfan, respectively. Pandit, et al. [105] studied the monitoring of residue levels of OCPs in costal marine environment of Mumbai. The concentration of total HCHs in seawater varied from 0.16 to 15.92 ng l⁻¹ and concentration of total DDT varied from 3.01 to 33.21 ng l⁻¹. The total HCH concentration in sediment was in the range of 3.8 to 16.2 ng g⁻¹. In sediment samples the DDT has higher mean concentration in comparison to its metabolite DDE and DDD. Leong, et al. [106] determine the level of selected OCPs in the water samples collected from Selangor River in Malaysia during 2002 to 2003. The OCPs detected were lindane, heptachlor, endosulfan, dieldrin, endosulfan sulphate, o, p'-DDT, p, p'-DDT, o, p'-DDE and p, p'-DDE. At the river upstream where a dam is located for public water supply, incidents of pesticide levels exceeding the European Economic Community directive of water quality standards have occurred. Ize-lyamu, et al. [107] determined the levels of OCPs residues in water and fish from some rivers in Edo state, Nigeria. In all the water sample analyzed, the OCPs residues determined (p, p'-DDD, p, p'-DDE, p, p'-DDT, o, p'-DDD, o, p'-DDT, lindane and aldrin) were presented, except in Ikoro river. The OCPs residues detected in water were also present in the fishes but at higher concentration. Imo, et al. [108] investigated the

contamination of OCPs from the selected rivers (Aja River, Asato River, Houtoku River, Kokuba River and Okukubi River) in Okinawa Island to estimate the current status of pollution in water, plants and surface sediments in these rivers. The concentration of total OCPs residues were in the range of 0.94-231.8 ng l⁻¹ in river water, 0.006-191.6 ng g⁻¹ dry weight in river sediments and 0.001-55.8 ng g⁻¹ dry weight in plants. Poolpak, et al. [109] measured the concentration of twenty OCPs residues in surface sediments collected from the tributaries of the Mae Klong River during 2003-2005. Total concentrations of OCPs found were ranged from 4.12 to 214.91 µg g⁻¹ dry weight in the first year. In the second year, total residue concentrations in the surface sediments were in the range of 3.26-215.09 µg g⁻¹ dry weight. Heptachlor epoxide was the contaminant found at highest concentration in this study. In addition, the occurrence of some selected contaminants including DDT, DDD and DDE reflects the recent contamination in the study area. Carvalho, et al. [110] determined OCPs residues in water, sediment and bivalve mollusk samples in the Mekong river delta, Vietnam. Chlorinated compounds, such as DDT, HCH and endosulfan, were detected in sediments and biota. The highest concentration measured were of DDT with an average of 6.3 ng g⁻¹ dry weight in sediments and 38.6 ng g⁻¹ dry weight in molluscs' soft tissues. Residues of OCPs originate from local usage of agrochemicals although with a likely contribution also atmospheric deposition of residues originated elsewhere. Adeyemi, et al. [71] measured OCPs residues in fish samples from Lagos lagoon, Nigeria. The mean concentration of OCPs ranged from 0.01-8.92 ppm. The concentration of OCPs (except for HCHs) in fish samples in this study were below the extraneous residue limit of 5 ppm, set by the codex alimentarius commission of FAO/WHO (1997). Carvalho, et al. [111] determined OCPs residues in water, sediment and biota samples collected from Laguna de Terminos, a protected area of the coast of Campeche, Mexico. Residue of chlorinated compounds were present in sediments and in biota with ΣDDT averaging 190 pg g⁻¹ and 5876 pg g⁻¹ in sediment and oysters, respectively. Results show that the more widespread contaminants in the Laguna were residues of chlorinated hydrocarbon, such as DDTs, endosulfan and lindane. Kalyoncu, et al. [112] measured the level of OCPs in 18 fish species from Konya markets, Turkey. DDT and its metabolites and HCH were the predominant contaminants in fish muscles. The mean concentrations of ΣDDT were in the range between 0.0008 and 0.0828 µg g⁻¹. Detectable levels of HCH, aldrin, and heptachlor were found in most samples. The mean of endrin ranged from 0.0040 µg g⁻¹ to 0.0326 µg g⁻¹.

Hoai, et al. [113] investigated the occurrence, temporal trend, sources and toxicity of OCPs in sediment samples from the sewer system of Hanoi city, Vietnam, including the rivers Nhue, To Lich, Lu, Set, Kim Nguu and the Yen So Lake. The concentration of DDTs, HCHs

and HCB ranged from 4.4 to 1100, < 0.2 to 36 and < 0.2 to 22 ng g⁻¹ dry weight, respectively. DDT/DDE ratios, indicating very recent inputs into the environment although these persistent compounds are banned in Vietnam since 1995.

OPs pesticides have been used for agricultural purposes for at least 50 years. Since the OCPs have been withdrawn from registered use because of the mounting evidence of their toxicity, persistence, and bioaccumulation in the environment, the OP pesticides are currently the largest and most versatile class in use. These compounds can be as toxic or even more toxic to humans and to aquatic life than any other kind of pesticide [114]. Their propensity for relatively short persistence, due to chemical and biological degradation, favour their usage. Although many OP pesticides are short-lived or are metabolized by the animals that ingest them, some are persistent and when applied in large amounts pervade the environment. OPs are generally acutely toxic. However the active ingredients within the group possess varying degrees of toxicity.

Minton and Murray [115] have divided OPs into three groups. The first most and toxic group, e.g. chlorfenvinphos, has a LD50 in the range of 1-30 mg/kg, the LD50 range for the second group, e.g. dichlorvos, is 30-50 mg/kg, and the least toxic group, e.g. malathion has a range of 60-1300 mg/kg. OPs work by inhibiting important enzymes of the nervous system which play a vital role in the transmission of nerve impulses. When exposed to OPs, the cholinesterase enzyme is unable to function and a build-up of acetylcholine occurs, which causes interference with the nerve impulse transmission at nerve endings [116]. In humans, poisoning symptoms include: excessive sweating, salivation and lachrimation, nausea, vomiting, diarrhea, abdominal cramp, general weakness, headache, poor concentration and tremors. In serious cases, respiratory failure and death can occur [3]. OPs kill insects by interfering with the nervous system function. Normally, impulses are transmitted chemically from the end of one nerve cell to the beginning of another; one of the chemical transmitters used in animal nervous systems is called acetylcholine. After transmitting the nerve impulse, acetylcholine is destroyed by an enzyme called acetylcholinesterase (AChE) in order to clear the way for another transmission. The OPs attach to AChE and prevent it from destroying acetylcholine, causing over stimulation of the nerves [3]. When a pesticide is applied, much of it reaches the soil. Water of streams and rivers, lakes and underground aquifers become contaminated from direct application, drift, run-off from treated areas, or waste materials. Pesticide residues in water, sediment and fish from different areas of the world have been described in many studies for instances; Brunetto, et al. [117] determine OPs pesticide residues in some watercourses from Mérida Province, Venezuela. Levels from < 0.3 to 16.5, < 0.1 to 12.2, < 0.2 to 4.1 and < 0.1

to 0.9 $\mu\text{g L}^{-1}$ of dimethoate, diazinon, methyl parathion and methamidophos were found. The pesticides most frequently detected were dimethoate and diazinon (89% of samples), followed by methamidophos (39%) and methyl parathion (33%). In general, waters contained pesticide concentrations reflecting local usage derived from agricultural activities.

Readman, et al. [118] determine the OPs pesticide residues in sediment samples collected from tropical marine environment in México. Of the OPs compound screened for, only chlorpyrifos was commonly encountered in sediments from the sampling region. Concentrations of up to 34 ng g^{-1} dry sediment were recorded, with highest levels in areas known to be subjected to agricultural runoff. Traces of parathion were, however, also observed in some samples. Miliadis [119] studied the environmental contamination of natural waters of Greece by pesticide residues. Thirty three water samples were collected from different rivers and lakes of Greece for determination of OPs pesticide residues. No OPs pesticide residues were detected in any water samples. Miliadis and Malatou [120] monitored the pesticide levels in natural waters of Greece.

Eighty water samples were collected from different rivers and lakes of Greece for determination of OPs pesticides. Pyrazophos, azinphos ethyl, malathion and diazinon were founded in water samples. Mortimer [92] quantified OPs pesticide residues in intertidal burrowing crabs *Australoplax tridentate* and a portunid *Scylla serrata* sampled from estuaries on the east coast of Australia between Cairns and Brisbane, Australia. Chlorpyrifos was only detected in crabs in the urban Brisbane area. Rovedatti, et al. [121] monitor OPs pesticide residues in water samples of the Reconquista River, Buenos Aires, Argentina. The analyses were performed, in three sampling stations along 46 km of its course. OPs pesticides were found in no case. Sapozhnikova, et al. [68] determined the OPs pesticide residues in sediments and fish tissue samples collected from the Salton Sea, California, USA. All samples were analyzed for 6 OPs pesticides. Dimethoate, diazinon, malathion, chlorpyrifos and disulfoton varied from ≤ 0.16 to 9.5 ng/g dry weight in sediments and from ≤ 0.1 to 80.3 ng/g wet weight in fish tissues. Disulfoton was found in relatively high concentrations (up to 80.3 ng/g) in all organs from Tilapia and Corvina.

Ownby, et al. [122] determined OPs pesticide residues in water, sediment and fish samples at the Sparta, IL, USA, National Guard Armory. Samples were collected from fifteen lakes at Sparta, IL site. Parathion and diazinon were detected in water samples at four locations in winter 2002-03; with high concentration. Pazou, et al. [102] studied the contamination of sediment samples collected on nine locations along the Quémé River in Bénin by OPs pesticides. Chlorpyrifos was identified in the samples. Henry and Kishimba [104]

quantified OPs pesticide residues in Nile tilapia and Nile perch collected from fish landing stations in nine riparian districts on Tanzanian side of lake Victoria. The residue levels in the fish fillet were up to 0.003 mg/kg fresh weight (0.7 mg/kg lipid weight) of fenitothion. Leong, et al. [106] determined the levels of selected OPs pesticides in water samples from Selangor River in Malaysia between 2002 and 2003. OPs pesticides detected were chlorpyrifos and diazinon.

Carvalho, et al. [110] determined the level of some OPs pesticide residues in water, sediment and bivalve mollusk samples collected from the Mekong River delta. Diazinon and fenitothion were detected only in water samples. Carvalho, et al. [111] investigated the contamination by OPs pesticides in water, sediment and biota samples collected from the coastal lagoon of Laguna de Terminos, Campeche, Mexico. Chlorpyrifos was detected in water in concentration up to 72 pg L^{-1} . Some of the OPs pesticides, however, are present in the marine environment for an appreciable period of time, particularly associated with sediments. Their presence, however, gives some cause for concern as they may reflect sporadic discharges to the aquatic environment through the drains. Such discharge could cause fish kills. El-Gohary and Abdel Wahaab [123] recorded high level of OPs pesticide residues in water samples collected from Manzala Lake. Abou-Arab, et al. [124] studied the levels of some pesticides in imported fish samples of sardine and mackerel collected from Egyptian governorate. Dimethoate and malathion were found at high frequency level. However, a lower frequency was found with methyl parathion. Dogheim, et al. [39] monitored OPs pesticide residues in water and fish samples collected from Kafr EL-Ziate governorate. No OPs pesticide residues were detected in water and fish samples. Osfor, et al. [40] recorded OPs pesticide residues in water, sediment and fish samples collected from Manzala Lake and river Nile. Level of diazinon and malathion were significantly higher in sediment of Manzala lake, while the level of parathion was significantly higher in sediment of river Nile. Boury fish of Manzala Lake contained higher level of malathion. The result indicated that Manzala Lake and even river Nile which was used as control are heavily contaminated by organophosphorus compound (malathion, dimethoate, diazinon and parathion). Abbassy [125] reported that dimethoate and malathion were the highest OPs pesticide residues detected in water of Rosetta and Damietta branches of the Nile river during 1995/1997. Abbassy [43] determined OPs pesticides residues drained into north coast of the Mediterranean Sea, Egypt. Only dimethoate and malathion from 21 OPs compound analyzed were detected mainly during summer, autumn and early months of winter. This might be due to application of these pesticides extensively in Egypt during these seasons. El-Kabbany, et al. [44] determined OPs pesticide residues in some water supplies and agricultural land, in El-Haram, Giza, Egypt.

The concentration of OPS pesticides (chlorpyrifos, dimethoate and parathion) seemed to be low in water as compared to soil samples. The water monitoring study confirmed the presence of the OPs compound in El-Moheet drainage water (chlorpyrifos, parathion and dimethoate). Chlorpyrifos was detected in canal water (el-Zomer and abd-el-aal land). Mansour, et al. [46] reported that diazinon, dimethoate and malathion were detected in water samples collected from Lake Qarun during 1997/1998 at 2.6, 6.0 and 4.7 ppb, respectively. Mansour and Sidky [50] studied the contamination of water, sediment and fish samples collected from Lake Qarun and Wadi Ei-Rayan lakes (Egypt). Malathion and pirimiphos-methy were detected in the major components of Lake Qarun. Abdel-Halim, et al. [126] monitored the residue levels of OPs pesticides in the aquatic environment (water, sediment and fish) of the drainage canal surrounding a pesticide factory at Damietta governorate. Chlorpyrifos was dominated in all water and sediment samples. It was ranged from 24.5 to 303.8 and 0.9 to 303.8 ppb in water and sediment samples, respectively. Diazinon level was slightly similar to chlorpyrifos in fish samples. Sallam, et al. [56] determined OPs pesticide residues in sediment samples collected from different location of river Nile from Aswan to Damietta governorate during December 2004 to January 2005. North Egypt governorate recorded high concentration of OPs pesticide than that detected in Upper Egypt governorate.

Rashed, et al. [57] reported that OPs pesticide residues were detected in 20% of water samples and 30% of fish samples collected from ten locations at Giza governorate. Ethoprophos was dominated in water samples, while dichlorophos, methamidophos and malathion were dominated in fish samples. Malhat and Nasr [127] detected chloropyrifos, cadusafos, diazinon, prothiphos and malathion in fish tissues samples collected from El-menofiya Governorate at level below the maximum residue limit. The highest average amount of chlorpyrifos (9.38 ng g^{-1}) and malathion (8.31 ng g^{-1}) were detected in El-Embaby drain. Prothiphos were found in tissues collected from El-Sarsawia canal and Miet-Rabiha drain at mean concentration of 4.91 and 6.55 ng g^{-1} , respectively. Diazinon was only found in one fish sample that collected from El-Menofi drain at the level of 9.23 ng g^{-1} . Malhat and Nasr [128] monitored the levels of 14 organophosphorus pesticides in water samples from different tributaries of the Nile River in Egypt during periods of from June 2007-September 2008. In all water sample analyzed only chlorpyrifos-methyl (41.53 ng L^{-1}) and prothiphos (30.03 ng L^{-1}) were detected in only one water samples.

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